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Calcium Cyanamide from Hydrogen Cyanide and Lime

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1. References:

None.

2. Purpose of this Report:

Forwarded herewith as Enclosure 1 is E.R.D.E. (Explosives Research and Development Establishment) Report No. 8/R/49 - "Calcium Cyanamide from Hydrogen Cyanide and Lime" by A.W.H. Pryde and W.J. Watkinson, dated June 1949.

3. Comments:

The introduction of the Report is repeated for convenience herewith as follows:

"A paper by Franck and Reimann in "Zeitschrift für angewandte & Chemie, 1951", 572, claims high yields of Calcium Cyanamide from the reaction



It was decided to repeat their work from the viewpoint of establishing a possible economical large scale process but omitting nitrogen as a carrier gas for the HCN."

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E.R.D.E. REPORT No. 8/R/49

Calcium Cyanamide from Hydrogen Cyanide and Lime

By

A.W.H. Pryde and W.J. Watkinson

This report does not contain information of overseas origin

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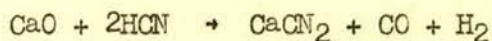
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Introduction

A paper by Franck and Heimann in "Zeitschrift für angewandte & Chemie, 1931", 372. claims high yields of Calcium Cyanamide from the reaction



It was decided to repeat their work from the viewpoint of establishing a possible economical large scale process but omitting nitrogen as a carrier gas for the HCN.

Experimental

An apparatus as shown in Fig. (1) was used. The essential features of this apparatus were:-

1. A silica tube of about $\frac{3}{4}$ in. bore and 30 in. long.
2. An electric furnace capable of maintaining a reaction of about 1 foot of the tube at controlled temperatures in the range 400 to 900°C.
3. A glass tube fitted with ground glass joint and stopcock for holding liquid HCN.
4. A series of absorption bottles containing 10% KOH for the absorption of unused HCN.
5. An aspirator in which to collect the residual gases.

The method employed was as follows:-

Anhydrous liquid HCN was prepared by the action of dilute sulphuric acid on potassium cyanide, the HCN being dried by passing it over Calcium Chloride and Phosphorous Pentoxide and finally redistilling. Condensation was achieved with an ordinary Liebig water jacket condenser and a cooled receiver. The HCN was stored in glass-stopped bottles at low temperature (BP. 26°C) until required.

HCN was introduced into the small glass cylinder, the stopcock closed, and the whole cooled and weighed. The weighing was repeated at the end of the experiment, thus giving the usage of HCN.

The silica tube was fitted at each end with a rubber bung and glass delivery tube. Rubber bungs were used for convenience and gave no serious difficulties at the temperatures used. The lower end of the tube was packed for about 6 in. with broken silica. The purpose of this was to raise the level of the lime to about the centre of the furnace and keep the lower bung and joint away from the heat. The cooling coil as shown in the figure fitted to the top of the tube was simply a length of "lead" pipe wound tightly round the tube and through which passed cold water. Its main purpose was to cool the issuing gases, and it also served to keep the upper joint cool. However, it was abandoned after a few runs as unnecessary with a long silica tube. The gases issuing from the top of the silica tube were passed through two scrubbing bottles

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containing 10% KOH to remove unchanged HCN from the issuing gases, and were finally led into a large aspirator. A point for gas sampling was fitted between the KOH bottles and the aspirator. The flow of gas through the apparatus was controlled by the flow of water from the aspirator.

The temperature of the furnace was measured by means of a thermocouple.

Lime, usually about 20 gms. was placed in the silica tube above the broken silica and the tube adjusted so that the lime was at the centre of the furnace. Nitrogen was drawn through the system to sweep out air, the furnace temperature set, and the whole left to obtain equilibrium. High melting-point vacuum-wax was found useful for sealing small leaks in the system.

Gaseous HCN was passed over the lime by raising the temperature of the water surrounding the HCN to about 30-35°C.

At the end of a run, the HCN tube was cooled and the apparatus swept clear with Nitrogen.

The first few runs were made at about 800°C and a gas flow of about 9 litres/hour. . The product in the silica tube was found to be in two distinct and clearly defined strata. That nearest the point of entry of the HCN was caked and dark grey in colour. At the further end it was white and appeared to be unchanged lime. The lime between the two was sharp. Moreover, the grey portion was rich in CaCN_2 whereas the white portion was very poor in CaCN_2 . It appeared, therefore, that reaction between lime and HCN at 800°C was spontaneous, and travelled progressively through the mass.

The different coloured products were analysed separately, the cyanamide being precipitated as the yellow silver salt.

The unused HCN scrubbed out by the KOH was estimated by titration to turbidity with AgNO_3 or by Volhard's method, giving very similar results.

Table 1. gives the results of the first 4 runs.

The volume of gas collected in each case agreed closely with the weight of HCN used, and indicated no volume change throughout the reaction. Tests indicated the formation of CO and H_2 as stated by Franck and Heimann.

These preliminary runs showed the feasibility of such a process and indicated that high yields of quite high purity calcium cyanamide might be expected. The conversion of HCN was almost total and reactions seemed spontaneous on contact.

Runs were now made with the object of finding the optimum working conditions. For all these runs, the cooling coil was omitted from the top of the reaction tube. Also after run 8, the direction of flow of gas through the reaction tube was reversed so that HCN entered at the top and the residual gases led off from the bottom. The general arrangement of the apparatus was, however, unchanged. Analysis of the issuing gases confirmed the production of CO and H_2 alone in approximately 1:1 ratio.

Table 2 gives examples of these subsequent runs.

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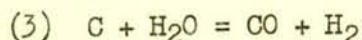
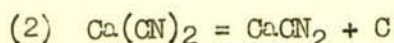
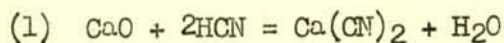
The results of Table 2 reveal the fact that whilst yield seems to depend solely on temperature, the particle size of the lime affects the purity of the CaCN_2 . This is probably due to reaction taking place first at the surface and then progressively through the particle. This was substantiated by the results in run 9 below.

A run was made using calcium carbonate in the form of precipitated chalk in place of lime in the reaction tube. Results are shown in table 3.

At the end of the test the reaction tube smelt strongly of ammonia. It seems therefore that with CaCO_3 other reactions take place involving the cracking of part of the HCN. This line of research was not continued.

To discover the approximate minimum temperature of reaction runs were made at 400 and 500°C, good yields of CaCN_2 having already been obtained at 600°C.

At 400°C, no CaCN_2 could be detected in the product, no gas was evolved and much $\text{Ca}(\text{CN})_2$ was present. At 500°C, a trace of CaCN_2 was found and also much $\text{Ca}(\text{CN})_2$. Thus it appears that the minimum economical reacting temperature lies between 500 and 600°C, probably closer to the 600° mark. Moreover, the presence of $\text{Ca}(\text{CN})_2$ at these lower temperatures and its absence at the higher temperatures tends to prove that the reaction proceeds in the following three stages:-



The effect of using metal reaction tubes was then investigated. With iron and stainless steel tubes much carbon was formed, and the residual gases contained a high percentage of H_2 and N_2 . This indicated cracking of some of the HCN. A copper tube, however, gave yields and purities comparable with those from a silica tube. The high thermal conductivity of the tubes made temperature control difficult and uniformity of heating was not obtained.

Table 4 gives the results from the series of experiments on metal tubes.

The following experiment was also instructive:-

Run 19. HCN at the rate of 5 litres per hour was passed through an iron tube containing lime in the form of lumps at 700°C. At the end, the lumps were black on the outside and were dark grey for a distance towards their centres, but had distinct white cores of apparently unchanged lime. This indicated that the reaction had proceeded progressively through the lumps. There was much free carbon in the tube and the gas analysis was as follows:-

O	-	nil
CO	-	40%
H ₂	-	48%
N ₂	-	12%

The HCN scrubbed out of the residual gas was extremely small (.016 gm. from about 7 gms. of HCN) bearing in mind the very free passage through the lime and tends to prove the cracking of HCN by iron at temperatures around 700°C.

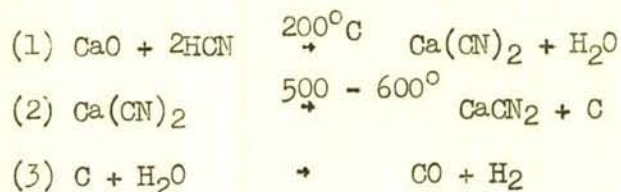
After the conclusion of this series of experiments, it was discovered that heating calcium cyanamide to 700°C in the presence of air caused a progressive decrease in the cyanamide content. Whilst endeavours were made to conduct all runs in the absence of air, the extreme importance of this factor was not appreciated at the time and it is possible that slightly better purities would be obtained if extra precautions were taken to exclude air at all hot stages, (specially during cooling) and to ensure the N₂ used for sweeping out was free from oxygen.

Heat of Reaction

The reaction is exothermic, $\Delta Q = -19.1 \text{ Kg.cals/gm.mol.}$

Conclusions

1. Calcium cyanamide in yields greater than 90% can be obtained from lime and HCN at temperatures over 600°C according to the equation $\text{CaO} + 2\text{HCN} = \text{CaCN}_2 + \text{CO} + \text{H}_2$.
2. Yields appear to depend solely on temperature of reaction.
3. Purity of product depends chiefly on the state of division of the particles of reactant. Purities greater than 90% may be obtained with suitably ground lime.
4. The minimum economical temperature of reaction lies between 500 and 600°C. Below 500°C no CaCN_2 is formed. $\text{Ca}(\text{CN})_2$ is present at lower temperatures indicating that the reaction proceeds:-



The darkness of the product can thus be explained by some of the water escaping before the carbon is formed, thus leaving excess C.

5. The use of calcium carbonate instead of lime introduces side reactions with the formation of ammonia and reduced yield.
6. Best yields are obtained in silica (or presumably some other ceramic) tubes. The use of iron tubes causes cracking of the HCN, with deposition of carbon, liberation of H₂ and N₂, and reduced yields. Copper tubes appear to have little cracking effect and give yields comparable with those from silica tubes.
7. Air or oxygen must be kept away from CaCN_2 at red heat.
8. The reaction between lime + HCN proceeds progressively through the mass leaving a sharp line of demarcation between the reacted and unreacted portions.

Recommendations

Should the manufacture of HCN on a large scale prove to be economic then the reaction between HCN and heated lime should prove a reasonable route to calcium cyanamide and should be further studied on a pilot plant scale.

TABLE I

Run	Reactant	Wt. Gms.	Temp. of Silica Tube °C	Temp. of HCN Bath °C	Wt. HCN used gms.	Rate of Gas flow litres/hr	% age original HCN recovered %	Max. Purity of CaCN ₂ %	Total CaCN ₂ Formed gms.	PER CENT YIELD		
										On original HCN %	% present in quantity not estimated	On un- recovered HCN %
1)	Pure	40	approx. 800	35	10.2	9	2.4	not est- imated				
2)	CaO 50% returned by 60BS Sieve	20	"	35	12.94	9	3.8	74.3	15.2	80		83
3)		20	"	28 - 36	9.32	6	3.9	55 (mean of total) 59.3	12	87		90.2
4)		20	"	35	10.47	9	2.8		11.84	76		79

TABLE 2

Run	Wt. HCN	Wt. Lime	Details of Lime	Rate of Gas Flow	Temp.	Durath. of Run	Gas Analysis	Wt. CaCN ₂ Formed
	gms.	gms.		Litres/hr	°C	hrs.		gms.
5	11.19	20	Pure CaO	8	600	1 $\frac{1}{4}$	-	14.9
6	14.55	20	50% retained by 60 B.S.S.	12	800	1 $\frac{1}{4}$	(O ₂ 0.3 CO 43.9 H ₂ 49.2 N ₂ 6.3 (by diff))	18.8
7	Excess	10		10	750	1	-	12.8
8	-	20		-	700	-	(O ₂ Nil CO 49 H ₂ 48 N ₂ 3 (N ₂ by diff))	-
9	10.54	15	ditto	9	700	1	(O ₂ Nil H ₂ 48 CO 48)	12.96
10	-	-	(Calcined pptd. chalk 200 BSS)	9	700	1	-	mean purity 71%
11	7.74	15	(Pure CaO passing 80 B.S.S.)	7	700	1	(O ₂ 3 CO 49 H ₂ 43 (N ₂ by diff) 7.7)	11.16
12	11.053	15	(Pure CaO Passing 150 BSS)	7	700	1		15.4
13	2.727	15	(Commercial lime passing 80 B.S.S.)	1	700	1 $\frac{1}{2}$	(O ₂ 1.5 CO 47 H ₂ 45.3 N ₂ 6.2 (by diff))	3.51
14	8.1	20	ditto	5	700	1 $\frac{3}{4}$	O ₂ 1.0 CO 45.6 H ₂ 51.2	11.03

TABLE 2

Wt. CaCN ₂ Formed	Max. Purity CaCN ₂	% Orig. HCN Recovd.	On Orig. HCN	On unrecvd. HCN	Remarks
gms.	%	%	%	%	
14.9	70.6	2.28	90	93	
18.8	60	5.05	87	93	
12.8	of 82% purity	(Total	Produced)		Excess HCN passed through
-	-	-	-	-	Ordinary run for gas analysis only
12.96	83.2	2.26	81.1	85.7	HCN Passed in from top
mean purity 71%	94	-	-	-	Very fine material to observe effect on purity
11.16	89.8	2.7	95.1	97.7	
15.4	92.3	3.09	91.7	98	
diff) 3.51	55.3	0.8	79.8	87.4	Flow too slow for experiment to mean much
11.03	89	1.85	92	94	Actual particle size very small probably < 200 BSS

TABLE 3

Run	HCN used	Temp.	Size of CaCO ₂	HCN recovered	Wt. CaCN ₂ formed	Max. Purity	Yield	
							On Orig.	On unrecovered HCN
15	4.74gms.	700-800° C	150 BSS	1.91%	2.91gms.	93%	41.4%	42.7%

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Run	Type of Tube	Reactant	Temp.	Wt. HCN	Rate of Flow	HCN Recovd.	Gas Anal
			°C	gms.	litres/hr	as at original	
14	Iron	Commercial lime passing 60 BSS	700 to 750	8.83	6	.06	O ₂ CO H ₂ N ₂
15	Iron	Ditto. Passing 80 BSS	700	9.66	5	0.06	O ₂ CO H ₂ N ₂
16	Iron	Pure CaO Passing 60 BSS	700	8.33	5	0.38	O ₂ CO H ₂ N ₂
17	Stainless Steel	Commercial lime Passing 150 BSS	700	8.15	5	11.8	O ₂ CO H ₂ N ₂
18	Copper	Pure CaO.50% retained by 60 BSS	700	6.616	6	0.5	O ₂ CO H ₂ N ₂ by <u>conc</u>

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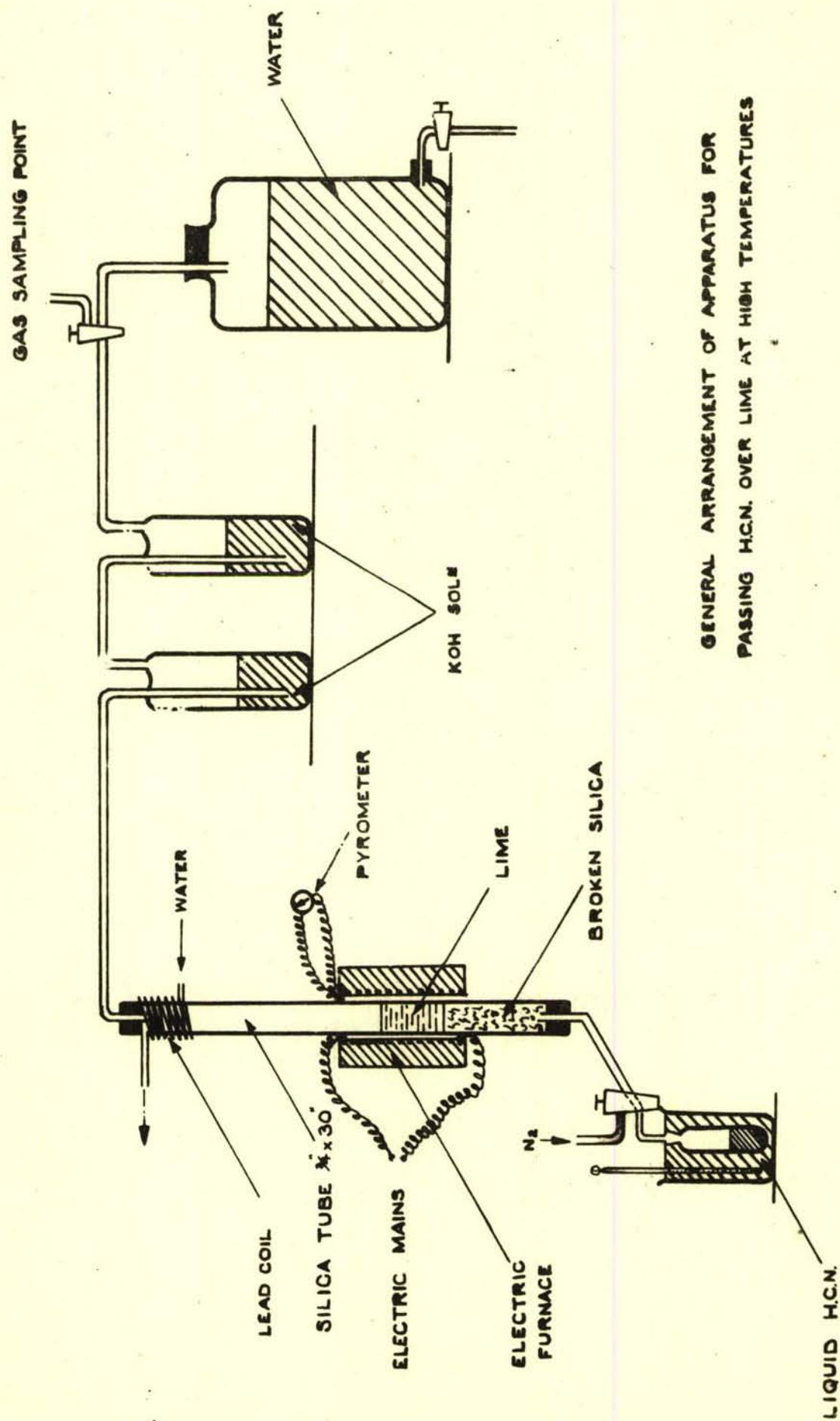
TABLE 4

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Ovd.	Gas Analysis	Max. Purity of CaCN_2 formed	Total CaCN_2 Formed	Yield		REMARKS
				on original HCN	On unrecvd. HCN	
Original			gms.			
1	O ₂ Nil CO 32 H ₂ 51.6 N ₂ 16.4	68.4	10.13	77.4	78	Much carbon formed in tube
6	O ₂ Nil CO 30 H ₂ 49 N ₂ 21	56.9	10.05	71	71	(much carbon formed. $\text{Ca}(\text{CN})_2$ present (calculated as CaCN_2). (Smell of NH_3)
8	O ₂ Nil CO 37 H ₂ 53.5 N ₂ 19.5	70	9.0	73	73.2	Much carbon present
3	O ₂ Nil CO 30 H ₂ 52 N ₂ 18	68.4	7.52	62	75.9	$\text{Ca}(\text{CN})_2$ present Calculated as Ca cyanamide
5	O ₂ Nil CO 42 H ₂ 58 N ₂ Nil All N ₂ S by difference	61	9.14	93.6	94.2	Product very similar to that from early experiments in silica tubes

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GENERAL ARRANGEMENT OF APPARATUS FOR
PASSING H.C.N. OVER LIME AT HIGH TEMPERATURES

FIG 1

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